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Evaluation of cryogenic agents cold energy in various phase states

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Abstract

It is thermodynamically possible to utilize a low-temperature potential of the media for generation of useful work. Such processes are usually met during re-gasification of liquid natural gas and hydrogen. These processes cause a question of how much energy can be generated by utilizing cold energy of the media. This article deals with evaluation of cold energy capacity of different fluids. Also, T-q2 diagram was suggested for estimation of the cold energy utilization efficiency.

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Keywords: *Cold energy; liquefied natural gas; heat of cryogen evaporation; cryogen*

1. Introduction

Currently, cryogenic fluids are widely used in various systems of aerospace technology, transportation, as well as in energy complexes of various purposes. The main advantage of using the gas at cryogenic liquid state is convenience of its storage and also transportation [1,2].

Cryogenic fuels and fluids are used in the following areas:

- aviation equipment;
- automotive engineering;
- technological processes in manufacturing;
- scientific research;
- biotechnology;
- cryomedicine.

An important condition for the application of cryogenic fluids is their storage and transport is taking into account their phase state. Cryogenic fluids may be in liquid, gaseous and solid state. In all cases, it is possible to use a low temperature potential of cryogenic fluid (material). Mechanism of the cold energy converting of cryogenic material is presented on the scheme, which is shown in figure 1. If cryogenic material is in the solid state, then it will execute a full cycle of conversations, which is presented by scheme «A-B-C». If cryogenic fluid is in the liquid state then

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cold energy conversion occurs by the scheme «B-C» (figure 1), and if cryogenic fluid is in the vapor state at cryogenic temperatures – then conversion goes only by the scheme «C»[3].

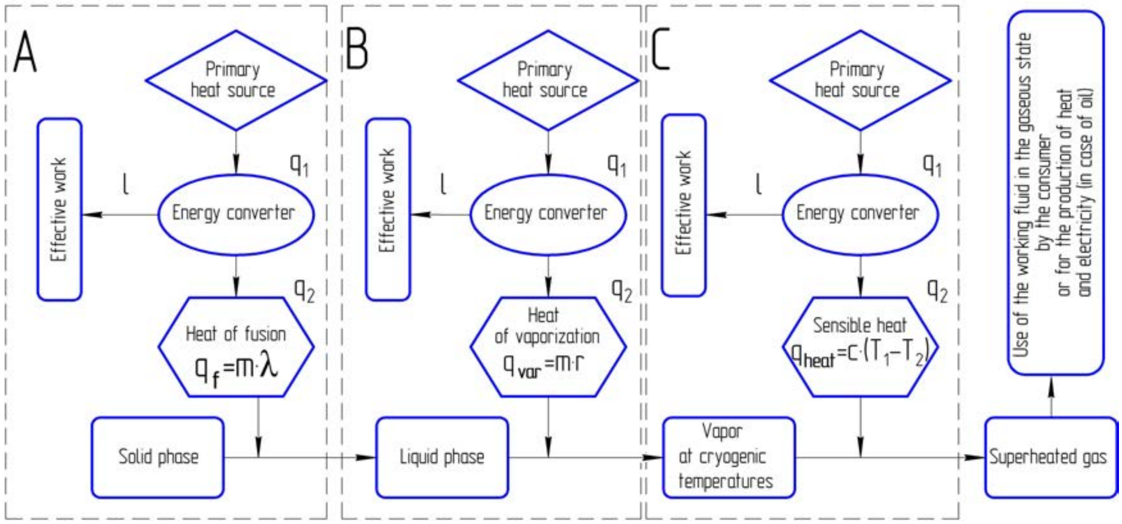

Fig.1. Cold energy conversion of cryogenic fluid (material) in the case of using the its maximum low temperature potential

2. Calculation of cold energy capacity of cryogen working agents

In accordance with the figure 1, it is clear that the energy potential of its phase transition (specific heat of fusion and heat of vaporization), the sensible heat, the chemical composition, the temperature and the pressure affect the usage efficiency of cold energy of cryogenic.[4-6]

The specific heat of fusion of cryogenic material depends on the pressure and chemical composition. At high external pressures, the fluid during expansion has to make significant work against external forces. Cryogenic materials expand during melting, and the specific heat of their fusion increases together with increase of the external pressure (except for ice, bismuth and gallium, which are not cryogenic materials).

Specific heat of vaporization of cryogenic fluid depends on its temperature and pressure. It is known that increase of the evaporation pressure leads to an increase of the boiling point. This reduces the specific heat of vaporization.

On the basis of analysis of reference data, the energy diagram of cold energy conversion of cryogenic fluids is plotted in the case of using its maximum low temperature potential at phase transitions for different fluids.

On the basis of obtained we will analyze the cold energy using of cryogenic fluid. Let fluid has the temperature T_2 = 20-150K and the ambient temperature T_1 = 250-300K. Thus, two different temperature levels allow to create the heat engine. The maximal efficiency of such a system by the Carnot cycle (figure 3) is defined as follows[7]:

$$\eta = 1 - \frac{T_2}{T_1} \tag{1}$$

$$\eta = \frac{l}{q_1} \tag{2}$$

$$l = q_1 - q_2 \rightarrow q_1 = l + q_2 \tag{3}$$

$$l = \frac{q_2 \eta}{1-\eta} \tag{4}$$

where η - thermal efficiency, q_1 – input heat to the energy converter from the environment, q_2 – cold energy of cryogenic fluid (rejected heat from the power converter), l – work output by the Carnot cycle.

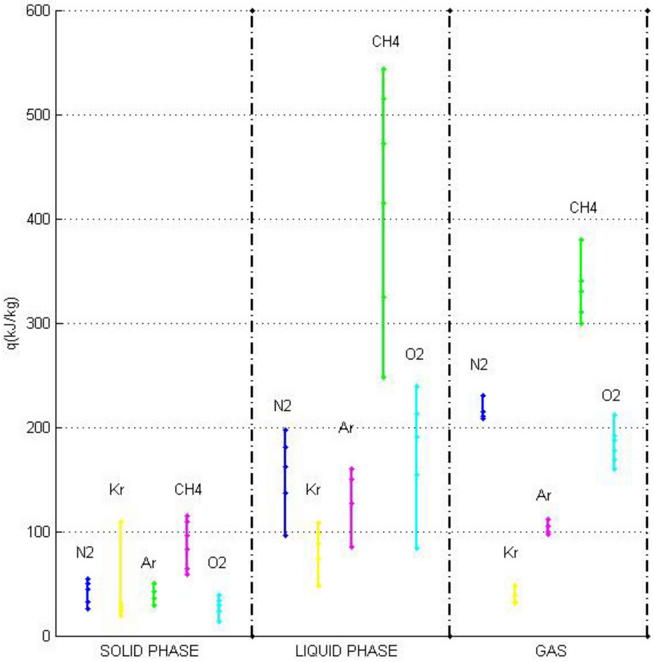

Fig.2. Available cold energy of various cryogenic fluids at its various phase states for pressure ranges presented in table 1

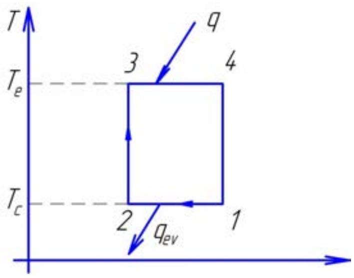

Fig. 3. – The using of available cold energy in the Carnot cycle as q_2

Simple calculations (expressions 1-4) for all of cold energy values of cryogenic fluids presented above at different phase states (figure 2) allows to get work output by Carnot cycle while using the latent heat of cryogenic fluid at various phase states as a lower heat source (figure 4). At obtained diagrams, the energy characteristics are shown in terms of using the fluids which are listed in Table 1.

The obtained data allows to apply them to solve the problems of increasing the energy efficiency of cryogenic systems by the use of cold energy.

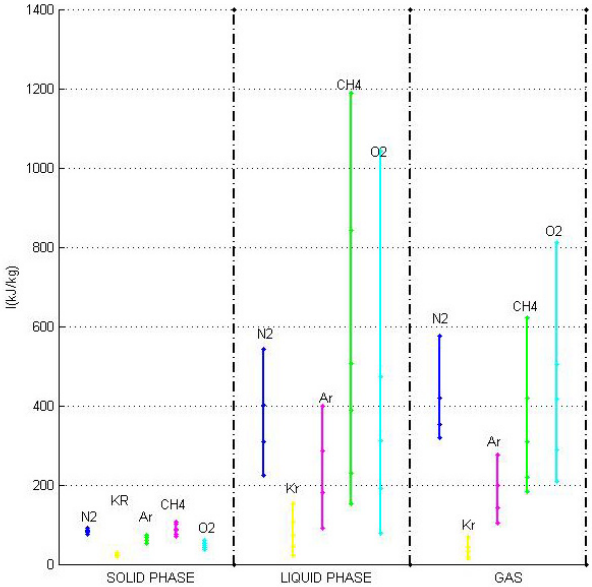

Fig.4. Work output by the Carnot cycle while using cryogen at various phase states as a lower heat source for pressure ranges presented in table 1

Table 1 - Thermodynamics parameters and processes characteristics of cold energy conversion at phase transitions for different fluids

Fluid	Characteristic	Solid phase	Liquid phase	Gaseous phase
Hydrogen (H_2)	$P_{min}...P_{max}$, MPa	0,1…54,6	0,09…1,1	0,09…1,1
	$T_{min}...T_{max}$, K	T=13,8...80	20...32	20...35
	q_2 , kJ/kg	58,6…338	419…921	35…400
	l, kJ/kg	1172,8…887,3	12433,5…3378,2	5400…2550
Nitrogen (N_2)	$P_{min}...P_{max}$, MPa	0,1… 3,0	0,17...2,52	0,17…2,52
	$T_{min}...T_{max}$, K	63...120	77,4...120	80...120
	q_2 , kJ/kg	25,5…54	95,7...197,6	208…219
	l, kJ/kg	91,9…76,5	542,8…224,2	574,9…319,6
Crypton (Kr)	$P_{min}...P_{max}$, MPa	0,1…2,4	0,1…4,22	0,1…4,22
	$T_{min}...T_{max}$, K	116,6…180	120...200	120...200
	q_2 , kJ/kg	19,5…30,1	47,8…107,9	31…48
	l, kJ/kg	29…18,4	152,9…21,5	68…14
Argon (Ar)	$P_{min}...P_{max}$, MPa	0,1...3,16	0,1…3,16	0,1…3,16
	$T_{min}...T_{max}$, K	83…140	83…140	83…140
	q_2 , kJ/kg	29,5…49,7	85,6…159,6	97…111
	l, kJ/kg	73,6…53,3	398…91,7	276,8…103,9
Methane (CH_4)	$P_{min}...P_{max}$, MPa	0,1...3,6	0,012…3,24	0,012…3,24
	$T_{min}...T_{max}$, K	90…180	91…180	110...180
	q_2 , kJ/kg	38,8...115,2	152...1188,3	300…380
	l, kJ/kg	86,2…70,4	1188,3…152	621,8…183,3
Oxygen (O_2)	$P_{min}...P_{max}$, MPa	0,1...4,0	0,01...4,2	0,01...4,2
	$T_{min}...T_{max}$, K	54...150	54…150 K	54...150
	q_2 , kJ/kg	13,9...39	83,9...23 8,7	160…212
	l, kJ/kg	60,7…36,4	1043,2…78,3	812.7…208

3. Calculation methodology of *T-q2 diagram*

In classical heat power plant with combined cycle a diagram is often used (figure 5) where he vertical axis means temperature and horizontal axis means high temperature potential (typically, enthalpy). The closer plots of exhaust gases temperature and water heating lies, the more efficiently plant operates from thermodynamic point of view.

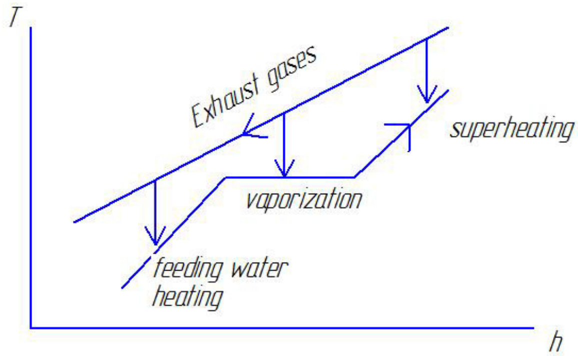

Fig. 5 – T-h diagram for power plant with combined cycle

It is possible to create a similar diagram for re-gasification process with is executed together with energy generation. In contrast with exhaust gas which are in the same phase during its temperature change, cryogenic fluids may change its phase during processes, so main line of the T-q2 diagram will not look like the line in classical diagram. Let's calculate a possible line positions on T-q2 diagram for methane because it is main component of liquid natural gas and regasification of LNG is most commonly used regasification process.

The algorithm of diagram design T-q_2 is as follows:

The starting point for the plotting of T-q_2 diagram is the point of the equilibrium state with the environment T_0, in which the low-temperature potential q_2 is equal to 0. By definition, for 1 kg of material[8]:

$$q_2 = \int_{\mathrm{T_x}}^{\mathrm{T_0}} \mathrm{c}_x \, dT. \tag{5}$$

This expression is valid for the single-phase medium heating with the substitution of the relevant thermal capacity.

For example, at the isobaric heating (all subsequent diagrams will be plotted specifically for the isobaric heating of cryogen) this expression is transformed into:

$$q_2 = \int_{T_x}^{T_0} c_p dT. \tag{6}$$

a) In view of this the cold energy curve is plotted either by integrating the equation (2) in accordance with the dependence of the thermal capacity vs. the temperature, or by dividing into sections and by the linear interpolation method. Values of cold energy potential are calculated for the temperature range: from ambient temperature to boiling temperature. And thus, until the boiling point.

b) Phase transitions are represented as isothermal processes, so that in T-q2 diagram such process is represented by a horizontal line at the temperature which is equal to the boiling point, and q_{liq}-q_{gas} = r, ie the difference between the low-temperature potentials of liquid and gas cryogen is equal to the heat of vaporization at a given pressure.

Thereafter the heating curve is plotted for the liquid phase similarly to paragraph (a), and then the phase transition of the liquid into solid is plotted accordance with paragraph (b), and finally, the curve ends by body heating, also similar to (a).

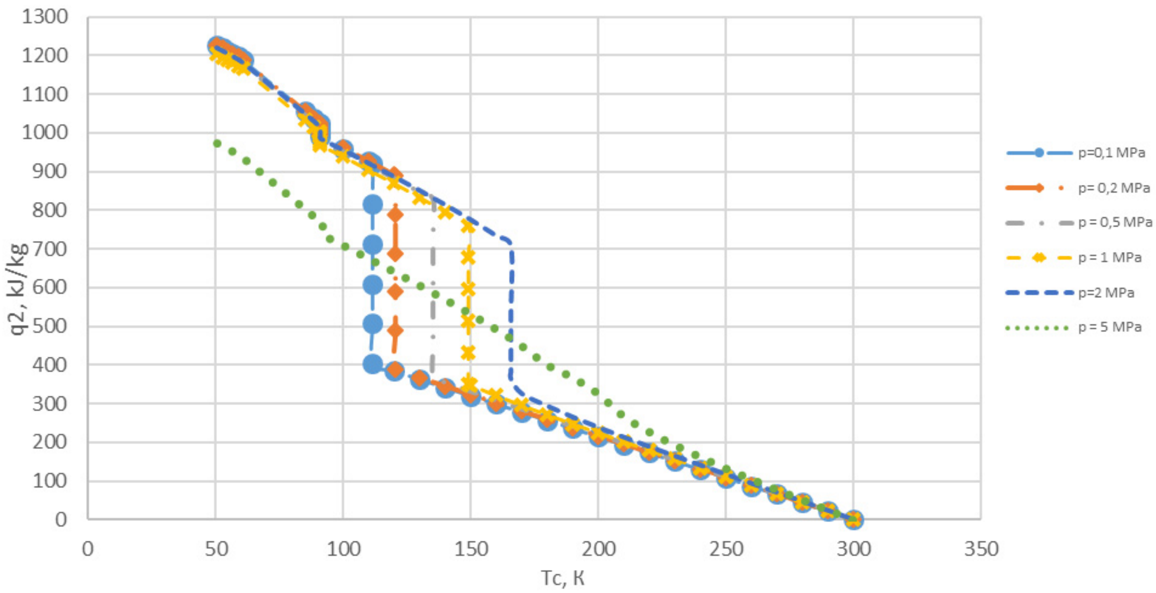

Fig. 6. T-q_2 diagram for methane.

T-q2 diagram for methane for pressure range from 0.1 to 5 MPa is presented on figure 6.

To estimate a efficiency of energy generation during re-gasification process, it is necessary to plot a T-q2 line for a pressure of re-gasification. Then, all temperature ranges of elements which utilize a cold energy are added to a diagram on the temperature levels, where they reject heat to a cryogenic fluid. Then by proximity of these plots to each other, it is possible to assess efficiency of cold energy utilization.

4. Conclusions

In this article, amounts of cold energy – energy of low-temperature heat which can be applied for energy generation was calculated for six fluids and various phases. Maximal work, which can be obtained by Carnot cycle utilization, was also calculated for these fluids.

The hydrogen has the highest cold energy capacity, which is not surprising due to its low vaporization temperature. The cold energy of methane as a part of luquid natural gas are most commonly used in existing re-gasification plants.

Method for cold energy utilization was also suggested which represents an analogue for T-h diagram which are used for estimation of power plant with combined cycle efficiency. Such analogue is T-q2 diagram, which were calculated and plotted for methane with different pressures.

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